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## Platinum Group Coatings for Refractory Metals

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<p>Oxidation resistant coatings of iridium on rhenium substrates have been produced by chemical vapor deposition from an iridium acetyl acetate starting compound. The process results in rapid buildup of iridium. Heat treatment to near the melting point of iridium causes the iridium to wet and diffuse into the rhenium surface eliminating porosity and assuring good bonding. These coatings have provided oxidation resistance at temperatures of 1850 C in air. After twenty minutes there was no evidence of deterioration.</p>				
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## SUMMARY

Oxidation resistant coatings of iridium on rhenium substrates have been produced by chemical vapor deposition from an iridium acetyl acetonate starting compound followed by heat treatment. These coatings have been shown to provide oxidation resistance at temperatures near 2000°C in air for over 20 minutes. The process results in rapid buildup of iridium, .1 to .2 g/m<sup>2</sup>s. A complication is the apparent codeposition of a carbon compound with the iridium. The resulting deposit is porous and does not afford oxidation protection to the underlying rhenium. Subsequent heat treatment of the residue modifies the coating so it forms a tight oxidation resistant coating. Further investigation of deposition parameters would be valuable to see if the carbonaceous codeposit can be avoided. A promising approach is to search for a gas which reacts with the carbon compound and carries off this reaction product before it deposits on the substrate.

## BACKGROUND

Increased efficiency as well as reduction in mass and size can be achieved for rocket engines and gas turbines by operating at higher temperatures. Examples include the JPL fluorine/hydrazine thruster development program with throat temperatures in the 1500°C to greater than 2000°C temperature range, the space shuttle vernier thruster with maximum temperatures of 1400°C and a desired life of 1,000,000 seconds, the cruise missile turbine, automotive and other gas turbines, etc. In order to retain sufficient strength at temperatures above 1000°C refractory materials such as molybdenum, tungsten, tantalum, niobium, rhenium or carbon/carbon must be used to fabricate the parts to withstand these temperatures. These materials and their structurally important alloys have notoriously poor resistance to oxidation in the temperature ranges where their strength characteristics are vitally needed. Protection from the oxidizing environment, in the form of coatings, is crucial for achieving the goals of the aforementioned programs.

Currently the only effective materials available for oxidation protective coatings are silicide-based. These materials are not without their limitations. A phenomenon called "pest behavior" has been observed for silicides. At high and low temperatures these materials have good oxidation resistance, however, in intermediate temperature regions they often disintegrate in air. Additionally, due to the difference of coefficient of expansion between the silicide and the base metal, repeated temperature cycling results in cracking of the coating which allows oxygen to diffuse into the cracks and ultimately destroy the base material. The upper limit for silicide coatings is approximately 1400°C but at these temperatures evaporation of the coating is sufficiently high to limit its life due to the limited thickness available from today's technology.

New oxidation resistant coating materials and processes must be developed which will permit operation in the 500 to 2000°C temperature range. Not only must these materials survive at these temperatures, but they must last for extended periods of time without evaporating, cracking or spalling. Advancement in the technology of rocket engines and gas turbines depends on the development of new oxidation resistant protective coatings.

High temperature oxidation resistant coatings can be categorized as:<sup>1</sup>

- o Intermetallic compounds that form compact crystalline oxide layers (eg  $\text{Al}_2\text{O}_3$  on superalloys,  $\text{HfO}_2$  and  $\text{ZrO}_2$ )
- o Noble metals and alloys which either don't react with  $\text{O}_2$  (Au) or react slowly forming volatile oxides (Ir and Pt)
- o Intermetallic compounds that form glassy oxide layers (eg silicides, borides)
- o Alloy coatings that form compact oxide layers (Ni and Co based alloys)
- o Stable oxides that provide physical barriers (Cr)

Phase I of this contract was directed to investigating the second category, specifically iridium on rhenium. Rhenium is of interest for space craft thrusters. Rhenium melts at 3180°C and retains substantial strength at high temperature (96MPa ultimate strength, 55MPa yield strength at 1800°C). With proper heat treatment, rhenium is ductile at room temperature and is machinable. In oxygen above 600°C, it undergoes catastrophic oxidation with evolution of white fumes of  $\text{Re}_2\text{O}_7$  (BP=363°C).<sup>2</sup> However at still higher temperature, say above 2000°C, oxidation proceeds much more slowly. Hence for high temperature applications of rhenium, the intermediate temperature range must be traversed rapidly or an oxidation resistant coating must be provided. Iridium melts at 2442°C. It has a volatile oxide ( $\text{IrO}_3$ ) but its oxidation rate at 1200°C is a thousand times less than Re.<sup>3,4</sup> Iridium electrodeposited on tungsten from a fused-salt bath followed by a plasma-sprayed  $\text{ZrO}_2$  layer to prevent volatilization losses has exhibited low weight loss during a 9 hour, 1800°C oxidation test.<sup>5</sup>

For the present task, Ultramet proposed to chemically vapor deposit iridium on rhenium substrates and to test the oxidation resistance of such coatings.

## PROCEDURE

### Deposition Parameters

In any CVD process, the first step is to choose the starting compound of the desired metal. The considerations are efficiency (what fraction of the metal in the compound ends up depositing on the substrate), reaction (substrate) temperature and rate of deposit build-up. Metal halides are frequently employed. Unfortunately, for the platinum group metals, the volatilization and decomposition temperatures are too close to be useful.  $\text{IrF}_6$  has been utilized by Machlin<sup>6</sup> but the compound is unstable at ambient temperatures and deposition was very slow. We decided to try iridium hexafluoride, iridium trichloride hydrate, iridium carbonyl and tris-acetyl acetonato iridium,  $\text{Ir}(\text{C}_5\text{H}_7\text{O}_2)_3$  or IrAcAc for short. The first three are known to be unstable and possibly they had substantially decomposed by the time we utilized them. In any event no deposits of Ir were obtained. IrAcAc is a yellow-orange crystalline powder at 20°C. The triple point of IrAcAc is above one atmosphere, hence it evaporates by sublimation. At 260°C, its vapor pressure is 1mm. At 270°C in a vacuum, its evaporation rate is of the order  $1\text{g/m}^2\text{s}$ . According to reference 7, IrAcAc thermally decomposes to lustrous iridium at 290°C. The other dissociation products are not determined. Substrates were heated to various temperatures while exposed to IrAcAc vapors, Fig. 1. A silver-gray deposit was obtained at temperatures between 500 and 850°C. At the lower end of the temperature range, the rate of deposition was very low. At the upper end, the deposit was powdery and flaked off. The optimal temperature is around 700°C. The 700°C coating assumes a granular appearance. Under a microscope the surface consists of closely packed rounded humps of fairly uniform size.

The rate of deposition for the conditions:

- o substrate temperature 700°C
- o IrAcAc temperature 270°C

amounts to about .1 to .2  $\text{g/m}^2\text{s}$ .

The IrAcAc we used was supplied by Johnson Matthey, Inc., W. Deptford, NJ. Iridium content is 98 - 99% of theoretical (39.3%).

Our work plan called for repeating the work of Machlin<sup>6</sup>, depositing Ir on graphite from  $\text{IrF}_6$ . Delivery of this compound was so tardy that we had already been more successful depositing Ir from IrAcAc than had Machlin using  $\text{IrF}_6$ .

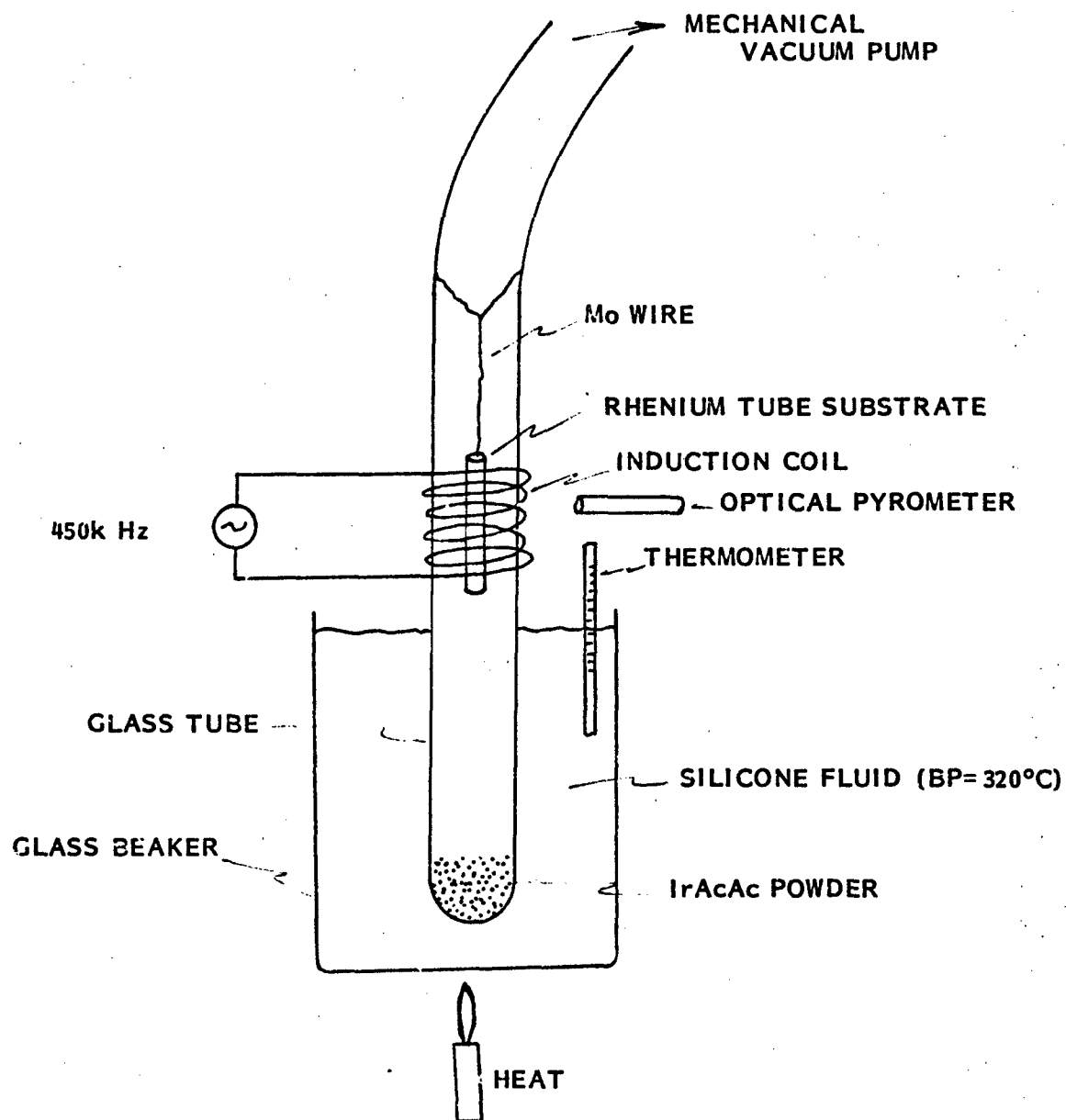


FIG. 1 SCHEMATIC OF CVD APPARATUS

## Substrate Preparation

The rhenium substrates used in this investigation were 3mm diameter tubes formed by chemical vapor deposition in the same way that rhenium thrusters are produced. After some coatings spalled off, we discovered that these tubes outgas profusely at high temperature. Subsequently we made a practice of out-gassing all substrates in vacuum at 2000°C before attempting CVD. This results in a microcrystalline (thermally etched) surface and seems to promote adhesion. Molybdenum rods 3mm in diameter were used as substrates during many of the runs where the deposition parameters were being optimized. Here again, adhesion was enhanced by high temperature thermal etching.

## Oxidation Tests

Oxidation tests were performed by induction heating the sample in air, to the desired temperature. The r-f output of our power supply restricted us to 2000°C or less, depending on the electrical resistance of the sample and the duration of the test. Because the specimens are tubes, and are not coated inside, we employed an apparatus which heated only the central regions and kept the ends cool in flowing argon, Fig. 2. In the case of rhenium, evidence of oxidation is quite dramatic. Dense white fumes of  $\text{Re}_2\text{O}_7$  are evolved in air at temperatures above 600°C. Since the oxide is volatile, oxidation is accompanied by a weight loss. At 1850°C, an unprotected tube is consumed in minutes. (See Fig. 3)

## Heat Treatment

Two types of heat treatment were employed. The first involved induction heating of the coated sample to 1800 - 2000°C to accelerate diffusion of the iridium and rhenium and improve the bonding of the two metals. We were able to perform this operation in the apparatus of Fig. 1. This was practiced before we were aware of the carbonaceous component of the coating. Fig. 4 shows the appearance of a typical specimen after 30 minutes at 1850°C.

To eliminate pinholes and porosity of the coating which resulted from the carbonaceous deposit, we began heating the coated specimens to 2440°C, the melting point of iridium, in vacuum. This caused the iridium to wet the surface of the rhenium and become very shiny. To attain such a high temperature necessitated placing the sample inside a hollow cylindrical graphite susceptor heated by an induction coil. The graphite furnace was insulated with graphite felt and was contained in a quartz chamber. To minimize carbon reactions with the sample, the latter was placed in a rhenium or tungsten crucible. A hole in the felt allowed a small area of the graphite susceptor to be visible to an optical pyrometer which was used to monitor the temperature.



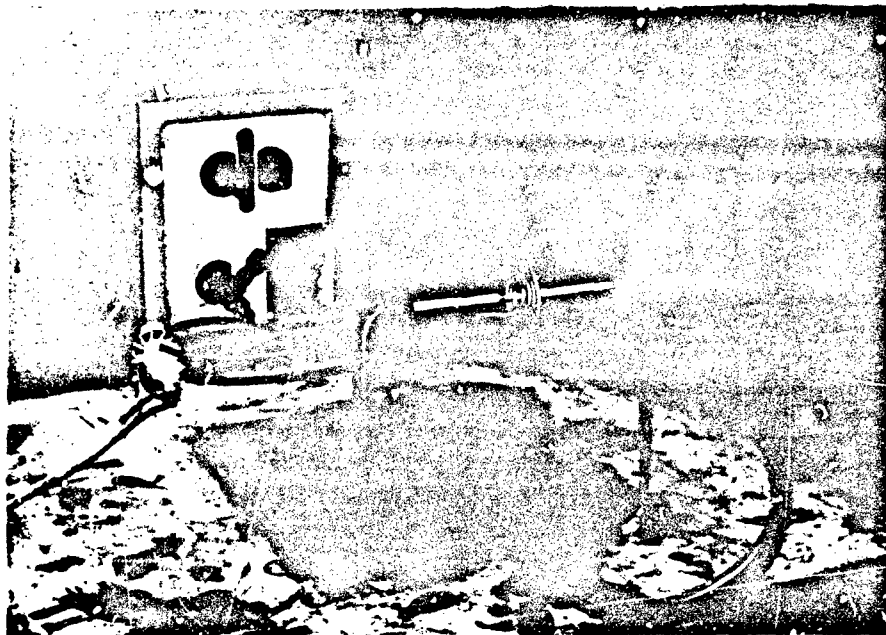


FIG. 2 PHOTO OF OXIDATION APPARATUS

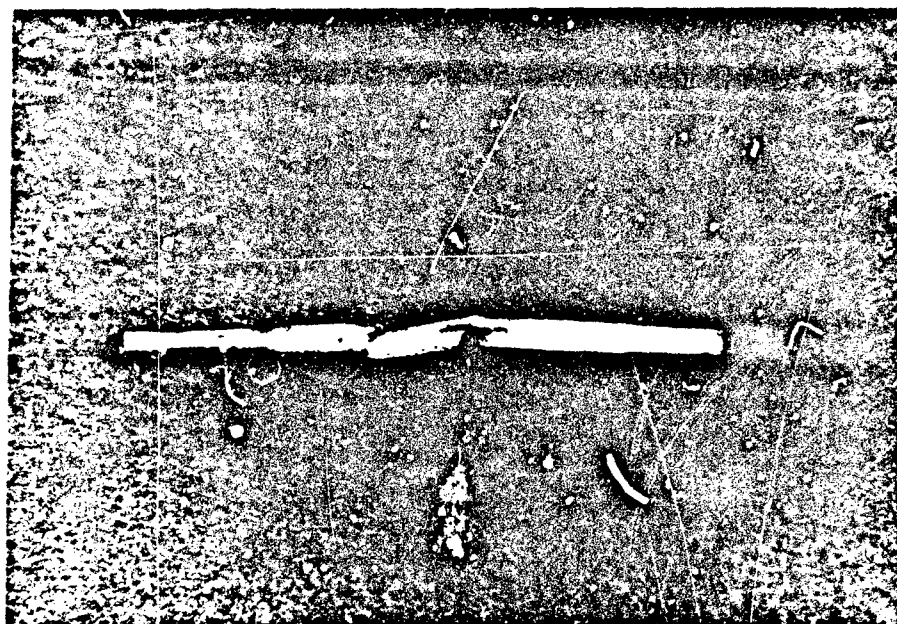


FIG. 3 PHOTO OF RHENIUM TUBE AFTER EXPOSURE TO  
AIR AT 1000°C

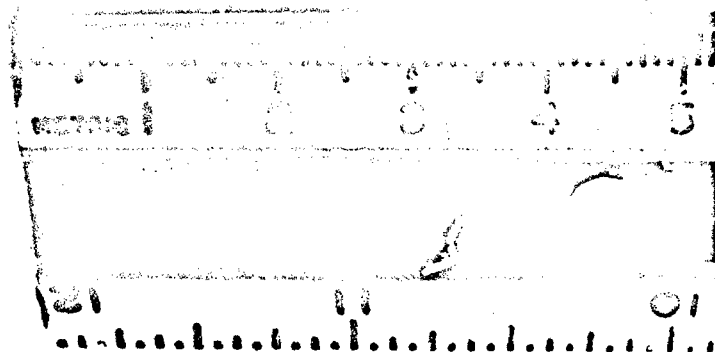


FIG. 4 IRIDIUM COATED RHENIUM TUBE AFTER HEAT  
TREATMENT AT 1850°C

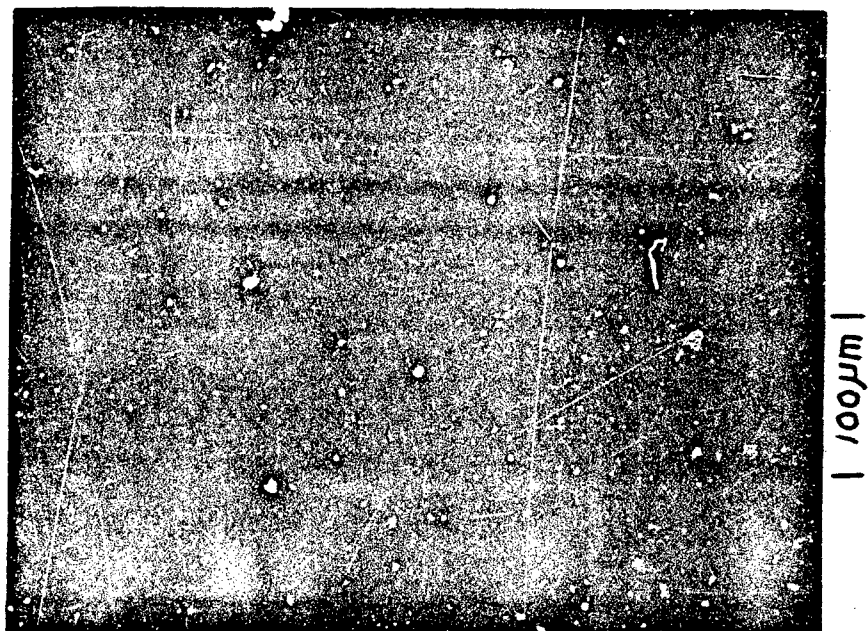
## RESULTS

Several dozen molybdenum rods and rhenium tubes have been coated with iridium by means of chemical vapor deposition from the starting compound tris-acetyl-acetonato-iridium, IrAcAc for short. Buildup is typically  $.1-.2\text{g/m}^2\text{s}$ . The deposit tends to be heaviest on the end of the sample nearest the vapor source. However, this is overcome by letting that end extend beyond the induction coil so its temperature is less than the  $700^\circ\text{C}$  or so experienced by the remainder of the sample. Coating thickness per run was typically 25 to  $75\mu\text{m}$ , limited mainly by the charge of iridium placed in the reaction chamber. Coatings as thick as  $200\mu\text{m}$  were obtained by multiple depositions, however there is no reason to believe that thick coatings could not be obtained in one continuous deposition providing there were sufficient charge. The fraction of the iridium in the charge which ends up on the substrate is .3 to .4, an efficient yield for CVD. That the deposit does in fact contain iridium was established by X-ray diffractometer analysis. Six prominent peaks were found to correspond to lattice plane spacings for iridium. That the deposit is not solely iridium is evidenced by the specific density of the coating which is typically 6 to 7 versus 22.4 for iridium. The iridium appears to be embedded in a matrix of carbonaceous deposit which is one of the reaction products of the thermal decomposition of IrAcAc. Following deposition, we heat the specimen to  $2400^\circ\text{C}$  with the result that the residue forms a silvery, adherent, non-porous coating on the rhenium. This has proved impervious to oxygen in subsequent heating to  $1850^\circ\text{C}$  in air for 20 minutes or more.

Two Ir/Rc specimens underwent the complete heat treatment including heating in vacuum to the melting point of iridium. These are the only specimens which exhibited significant oxidation resistance when heated in air. Following the oxidation tests, these samples, #16 and #19, were sectioned, mounted, etched and microphotographed. Two phases are evident in Figure 5 (part 16) and Figure 6 (part 19). The lighter region is the iridium coating, more precisely, it is an iridium rhenium alloy. The section thickness in each case is about  $250\mu\text{m}$ . It is evident that even after 20 minutes at  $1850^\circ\text{C}$ , the iridium layer is intact and presumably could continue to afford oxidation protection of the rhenium.

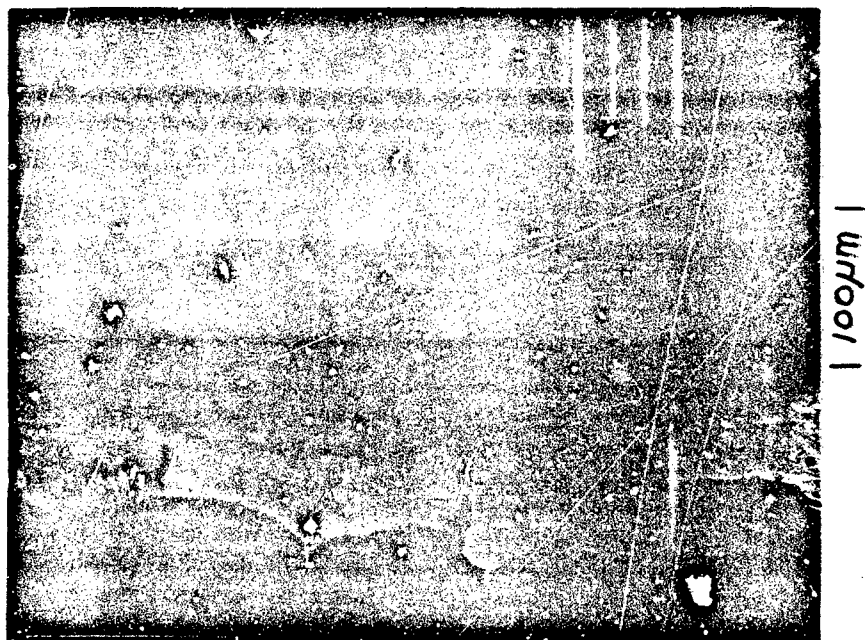
## CONCLUSIONS

The present work has demonstrated that it is possible to form a non-porous, adherent coating of iridium on rhenium, which protects the rhenium from oxidation at  $1850^\circ\text{C}$  (or more) in air. Chemical vapor deposition from tris-acetyl-acetonato-iridium results in rapid deposition of iridium, but also codeposits a carbonaceous compound which must be got rid of before the iridium can form a tight pore-free bond to the substrate.



LONGITUDINAL SECTION OF PART # 16

FIG. 5



CROSS-SECTION SEGMENT OF PART # 19

FIG. 6

## RECOMMENDATIONS

1. Further research needs to be done to discover a carrier gas which will combine with the carbon reaction products at or near the surface of the substrate and prevent their codeposition with the rhenium.
2. Longer oxidation tests at temperatures beyond 1850°C should be performed to discover the limits of protection.
3. Determine the oxidation resistance characteristics of iridium, rhodium and platinum. This is useful as baseline data to verify the available data and extend the range to 2000°C. Oxidation resistance can be measured by determining the weight and dimensional changes of solid samples. The oxidation resistance test facility fabricated in Phase I can be used for this purpose. In order to determine which material is best for a specific mission, this information is necessary.
4. Design, fabricate and test a facility for measuring oxidation resistance on the inside of tubular samples. Since oxidation resistant coatings for thrust chambers will be on the inside of the device, a geometry should be tested which more closely simulates actual operation.
5. Determine the deposition parameters required for the deposition of platinum and rhodium. Since platinum promises to be more oxidation resistant up to 1400°C, applications exist where platinum would be the best choice as an oxidation resistant coating material. Based on the knowledge gained from Phase I, platinum acetyl acetate should be the first material investigated. Other organometallics should be investigated if the acetyl acetate is not successful.
6. Extend the techniques learned in Phase I to depositing iridium and platinum onto additional substrates: molybdenum, columbium, nickel, and carbon/carbon. This includes direct deposition and using rhenium as an intermediate layer.
7. Assess the prospect of depositing a ceramic layer ( $ZrO_2$  or  $HfO_2$ ), on top of a platinum group metal coating as a method of inhibiting evaporation of the platinum group metal.
8. Modify the techniques developed in Phase I for plating outside surfaces to permit depositing iridium and platinum on the inside of tubular structures. Geometric effects of deposition require developing a different deposition mechanization for depositing on the inside of tubular structures than on the outside.

9. Do metallography of selected coated specimens to determine composition, grain morphology, defect structures and boundary conditions.
10. Measure the mechanical properties of the coated parts to determine whether any adverse effects on strength, ductility, etc. have occurred as a result of the oxidation resistance process.
11. Test the oxidation resistance of the various substrate/coating combinations. This will involve measuring the effects of temperature, thermal shock and temperature cycling.
12. Provide oxidation resistant coatings to rocket engine manufacturers for test under actual conditions.

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